



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# Comparison of Spectroscopic Data with Cluster Calculations of Plutonium, Plutonium Dioxide and Uranium Dioxide

J. G. Tobin, S. W. Yu, B. W. Chung, M. V.  
Ryzhkov, A. Mirmelstein

June 8, 2012

12th Russian-US Pu Workshop  
Oxford, United Kingdom  
July 20, 2012 through July 22, 2012

## **Disclaimer**

---

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

# Comparison of Spectroscopic Data with Cluster Calculations of Plutonium, Plutonium Dioxide and Uranium Dioxide<sup>#</sup>



**J.G. Tobin<sup>1\*</sup>, S.-W. Yu<sup>1</sup>, B.W. Chung<sup>1</sup>, M.V. Ryzhkov<sup>2</sup>, and A. Mirmelstein<sup>3</sup>,**

*<sup>1</sup>Lawrence Livermore National Laboratory, Livermore, California, USA*

*<sup>2</sup>Inst. of Solid State Chemistry, Ural Div. of the Russian Academy of Science, Ekaterinburg, Russia,*

*<sup>3</sup>Department of Experimental Physics, Russian Federal Nuclear Center,  
E.I. Zababakhin Institute of Technical Physics (VNIITF), Snezhinsk, Russia*

*\*Corresponding author: [Tobin1@LLNL.Gov](mailto:Tobin1@LLNL.Gov)*

*<sup>#</sup>[LLNL-ABS-529332](#), [LLNL-JRNL-524554](#), [LLNL-TR-516874](#), [LLNL-ABS-553772](#)*

***12<sup>th</sup> Russian-US Pu Workshop, Cambridge, UK, July 20-22, 2012***



# Overview of talk

---

- Motivation
- Description of instrumentation and data collection
- XAS, XPS, BIS of  $\text{UO}_2$ 
  - Occupied Density of States: XPS
  - XAS: O1s - old and new
  - XAS: U4f - new data vs previous EELS
  - XAS: U4d and U5d – old and new
  - Monochromator calibration → Unoccupied DOS
- ResPES and XAS of Pu
- Comparison of Experimental and Cluster Calculation Results
- Summary

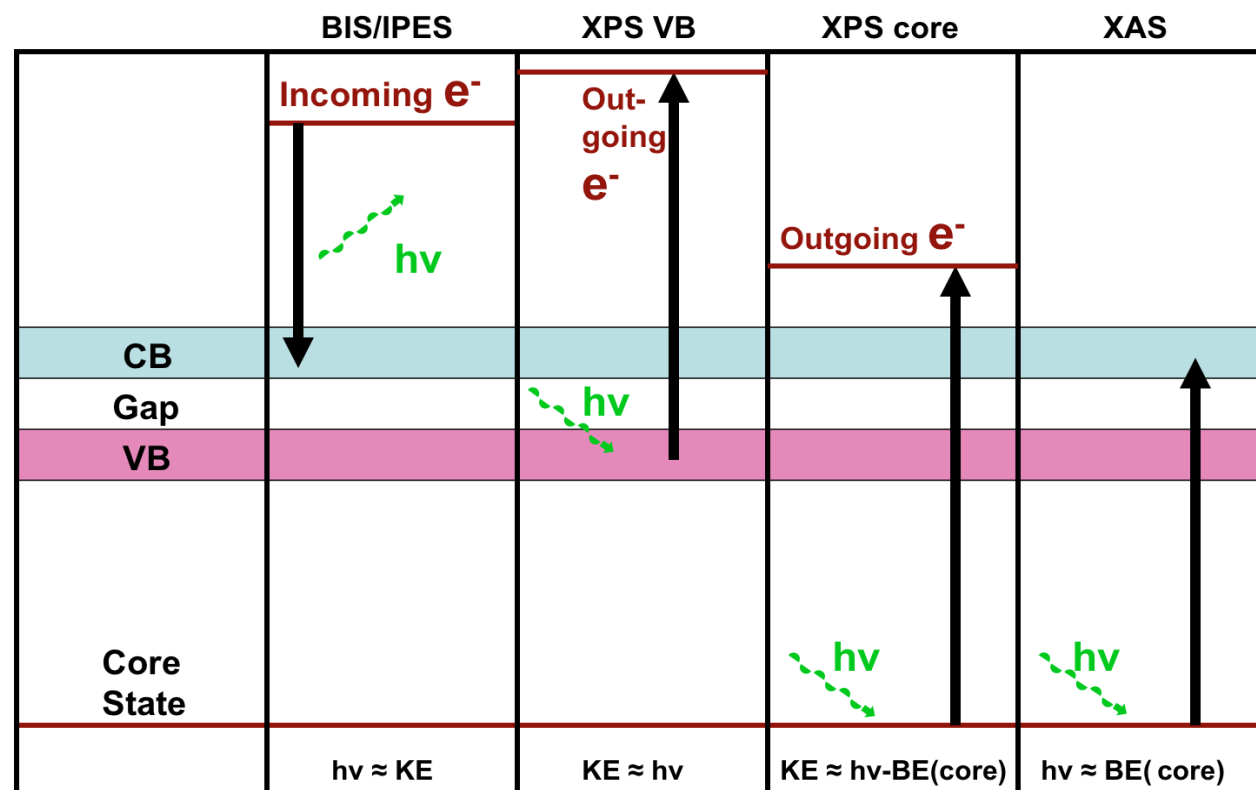
# Motivation and Instrumentation



Using spectroscopic data produced in the experimental investigations of bulk systems, including X-Ray Absorption Spectroscopy (XAS), Photoelectron Spectroscopy (PES) and Bremstrahlung Isochromat Spectroscopy (BIS), the theoretical results within for  $\text{UO}_2$ ,  $\text{PuO}_2$  and Pu clusters have been evaluated. The calculations of the electronic structure of the clusters have been performed within the framework of the Relativistic Discrete-Variational Method (RDV). The comparisons between the LLNL experimental data and the Russian calculations are quite favorable. The cluster calculations may represent a new and useful avenue to address unresolved questions within the field of actinide electron structure, particularly that of Pu. Observation of the changes in the Pu electronic structure as a function of size suggests interesting implications for bulk Pu electronic structure.

- Onsite Instrumentation: A spectroscopic system containing spin resolved photoelectron spectroscopy (SRPES) and bremsstrahlung isochromat spectroscopy (BIS) has been built and commissioned at LLNL.
- ALS Instrumentation: The XAS was done on Beamline 8 and Beamline 7. Both Total Electron Yield (TEY) and Total Fluorescence Yield (TFY) were used. TFY is less surface sensitive than TEY.

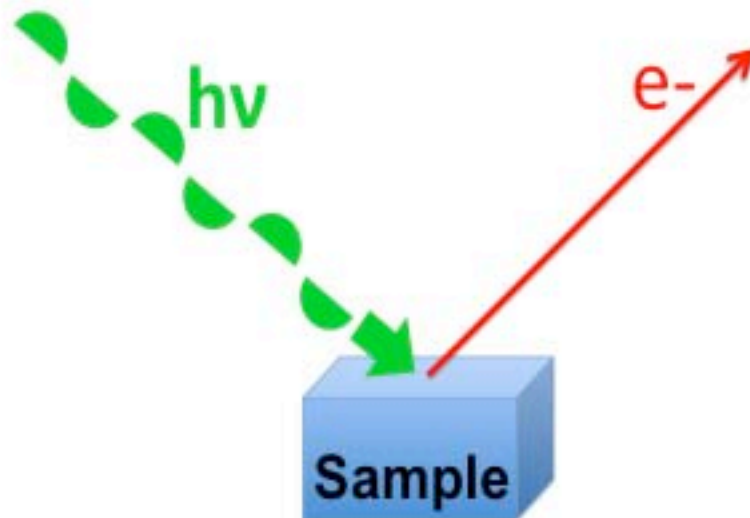
# Comparison of Processes: BIS, XPS and XAS



- XPS samples the occupied DOS or Valence Band (VB)
- BIS and XAS sample the unoccupied DOS or Conduction Band (CB)

**Photon absorption and emission:**  
**electric dipole transitions with  $\Delta l = \pm 1$**

# X-ray photoelectron spectroscopy (XPS) and Ultra-Violet photoelectron spectroscopy (UPS)



Select energy (and  
direction) of electrons

Laboratory Sources

AlK $\alpha$   $h\nu = 1487$  eV

MgK $\alpha$   $h\nu = 1253$  eV

HeI = 40.8 eV

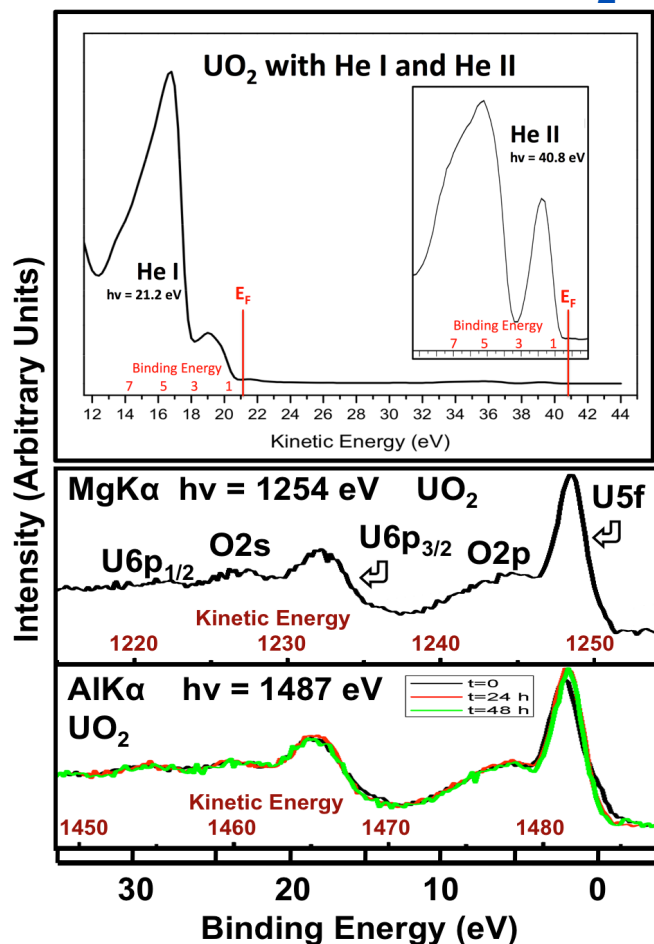
HeI = 21.22 eV

$$h\nu = KE_e + B^F + \Phi$$

# X-ray Photoelectron Spectroscopy (XPS) gives us the Occupied Density of States



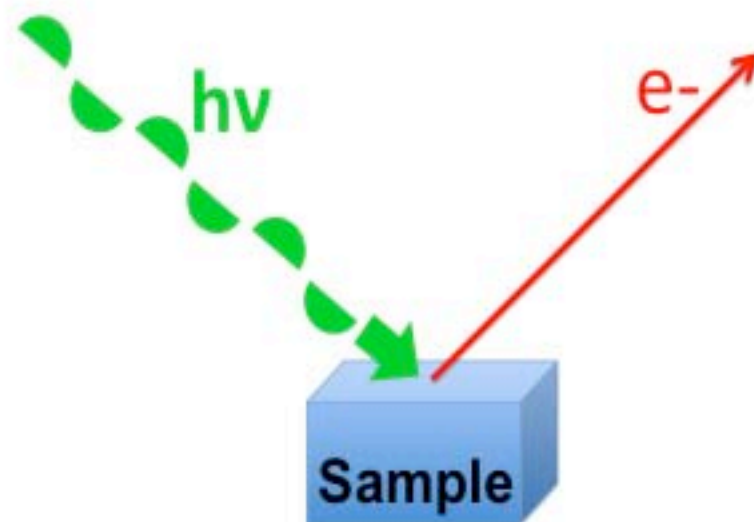
## UPS and XPS of $\text{UO}_2$



- The assignments here go back to Veal and Lam (1974) and are supported by other workers as well.
- B.W. Veal and D.J. Lam, Phys. Rev. B 10, 4902 (1974) and Phys. Letters 49A, 466 (1974).
- J.R. Naegele, "Actinides and Some of their Alloys and Compounds," Electronic Structure of Solids: Photoemission Spectra and Related Data, Landolt-Bornstein "Numerical Data and Functional Relationships in Science and Technology," ed. A Goldmann, Group III, Volume 23b, Pages 183 – 327 (1994).
- For the complete UPS and XPS study, see Yu and Tobin, JVSTA 29, 021008 (2011).



# Synchrotron-radiation-based photoelectron spectroscopy (PES), including Resonant PES or RESPES



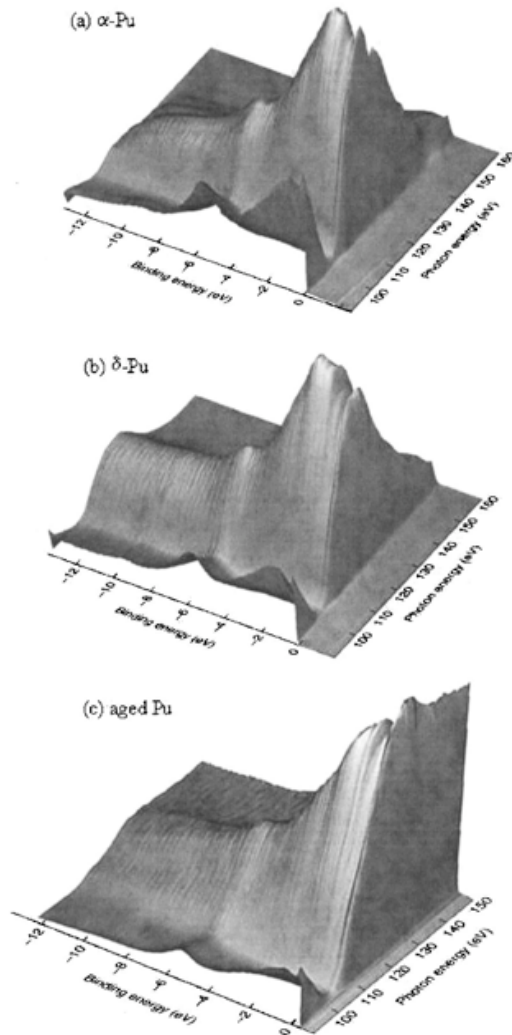
Select energy (and direction) of electrons

Tunable  $h\nu$  source

Thus, double monochromatization:  
Both  $h\nu$  and electrons.

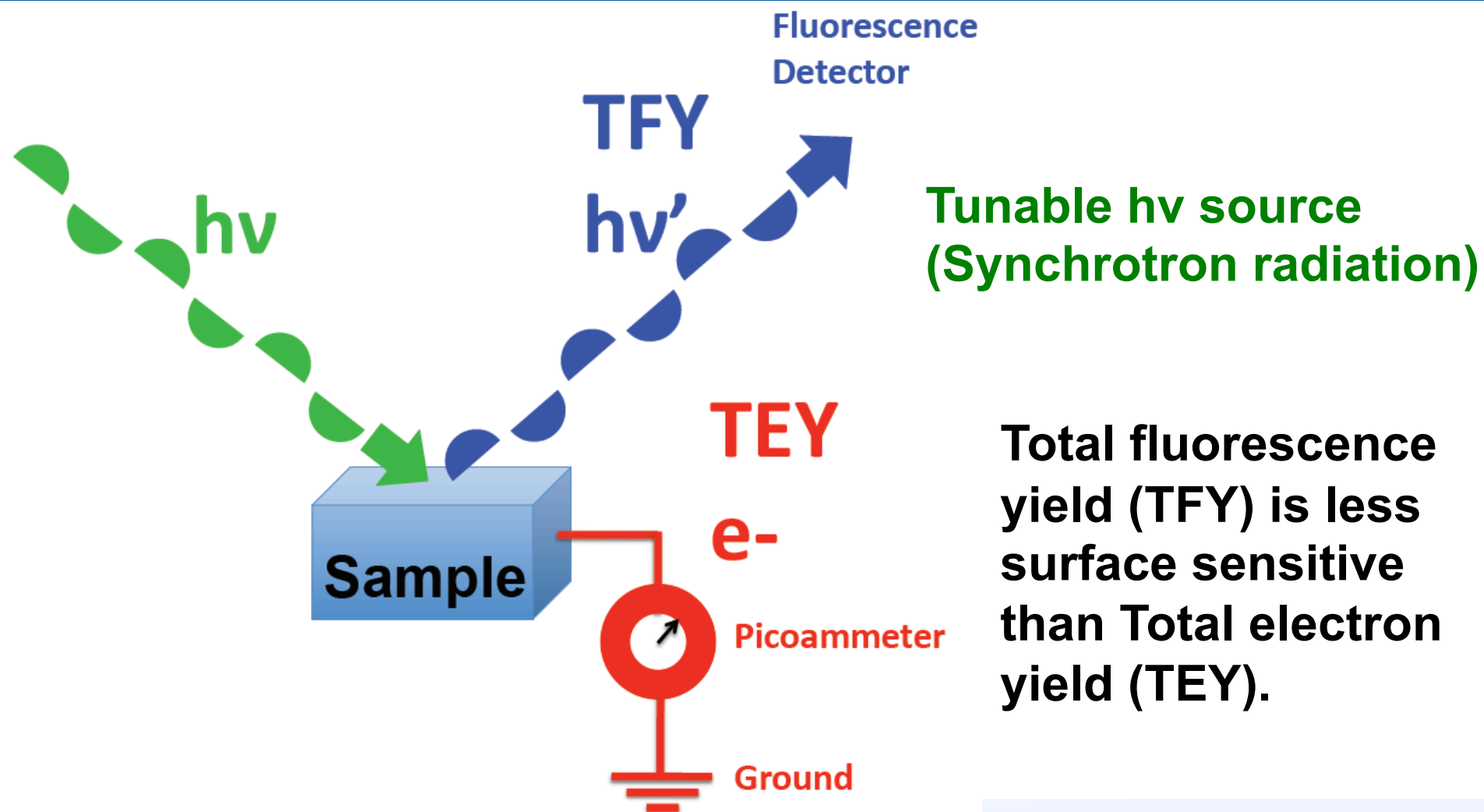
$$h\nu = KE_e + B^F + \Phi$$

# RESPES of Pu



- J. G. Tobin, B. W. Chung, R. K. Schulze, J. Terry, J. D. Farr, D. K. Shuh, K. Heinzelman, E. Rotenberg, G. D. Waddill, and G. van der Laan, Phys. Rev. B **68**, 155109 (2003)

# X-ray absorption spectroscopy (XAS)

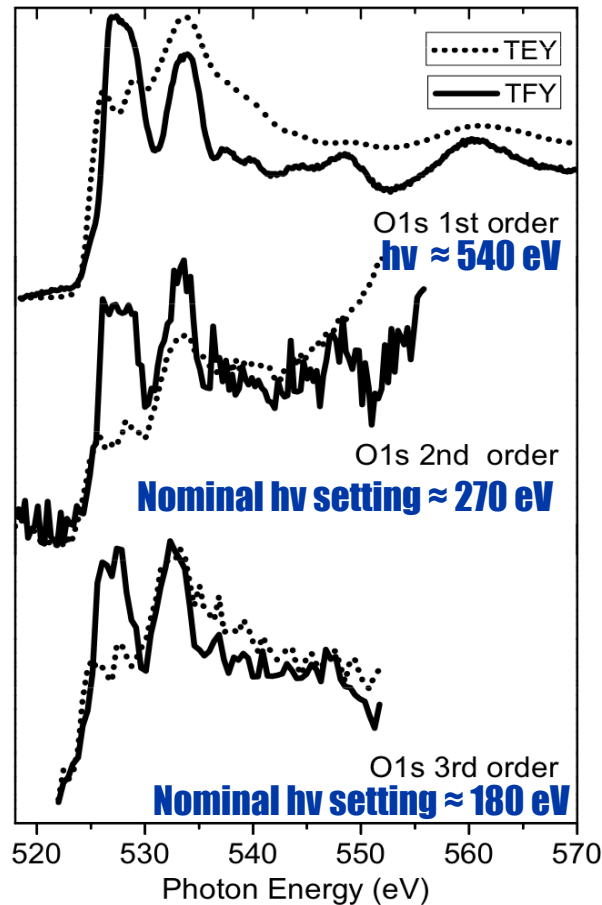


**Total fluorescence yield (TFY) is less surface sensitive than Total electron yield (TEY).**



# O1s XAS: old and new → O2p UDOS

## Our data in 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> Order



- Our TEY looks just like that from Jollet et al.
- However, TFY gives a better measure of the bulk electronic structure, that will be used instead.
- The three orders permit a quantitative calibration of the hv scale on the middle energy grating.
- All three orders agree...

## Jollet et al, JPCM 9, 9393 (1997)



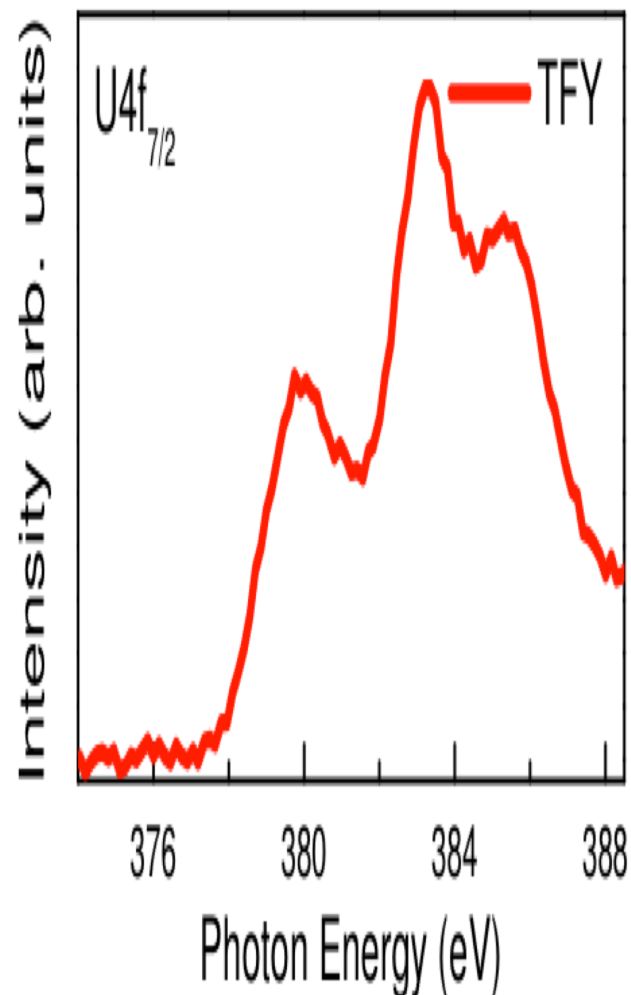
Figure 1. XAS oxygen K edge of  $\text{CeO}_2$  (a) and  $\text{UO}_2$  (b).

Table 1. Energies of the structures of the O K XAS spectrum for  $\text{CeO}_2$  and  $\text{UO}_2$ .

	a	b	c	d	A	B	C	D	E
$\text{CeO}_2$ (eV)	—	530.9	533.5	537.9	543.6	545.7	548.7	553.9	563.4
$\text{UO}_2$ (eV)	528.55	530.65	532.2	537.0	540.9	543.1	546.85	551.85	564.05

# U4f XAS new data agrees with EELS

## U4f XAS → U6d UDOS



- TFY shows a strong signal while TEY only shows the Nitrogen contaminant at 400 eV. This may be driven by surface contamination or cross section effects.

- Our 4f<sub>7/2</sub> XAS looks like the EELS of Moser et al.

- Using middle grating calibration from O1s

**EELS from Moser, Delley, Schneider and Baer, PRB 29, 2947 (1984)**

**They showed convergence to high KE limit : EELS = XAS**

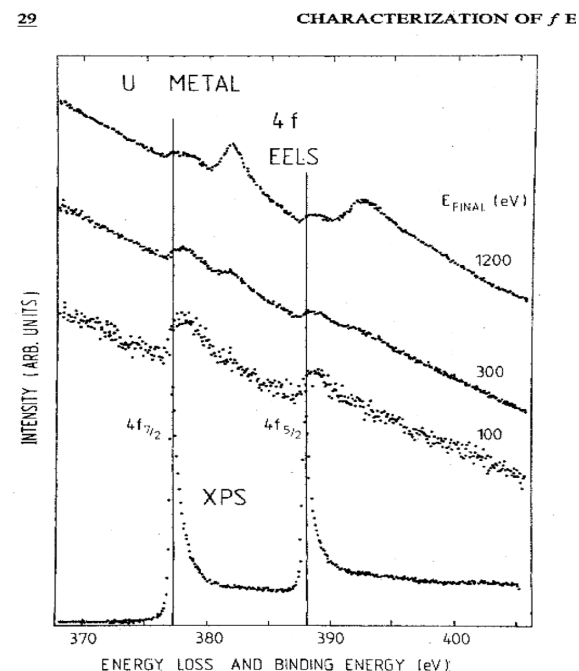
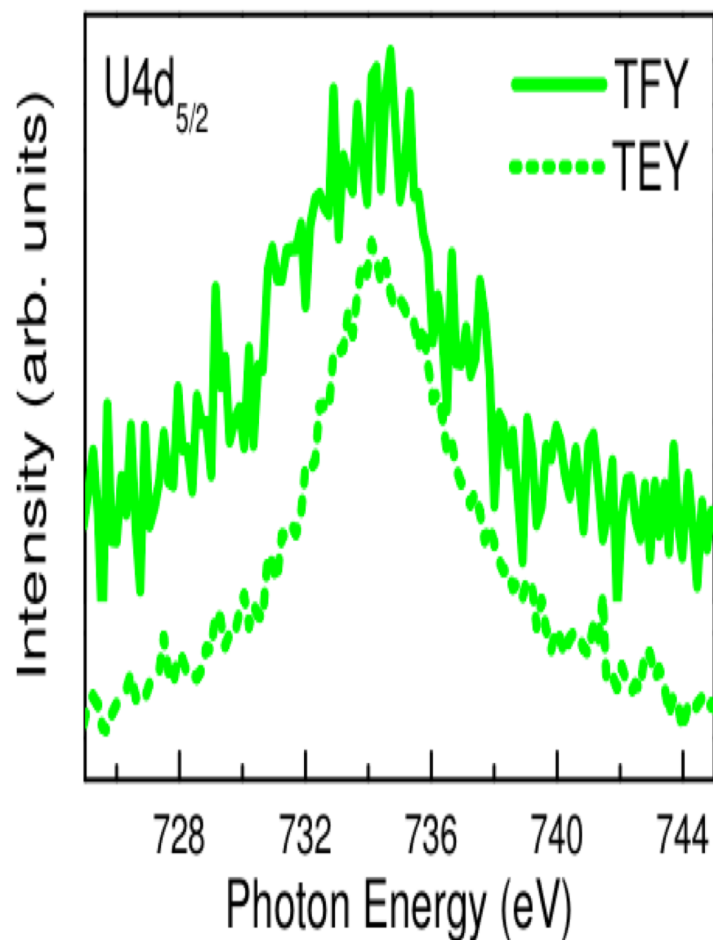


FIG. 3. EELS spectra, taken at the indicated final-state energies, and XPS 4f core-excitation spectra of U metal. The common onset of the EELS and XPS emission is indicated by the two parallel lines drawn through the maxima of the spin-orbit-split XPS components.

# U4d XAS: old and new → U5f UDOS, but broadened



- The  $U4d_{5/2}$  looks just like that of KKBK and the energy calibration of the high energy grating is dead on.
- The TEY and TFY are similar, but the TEY is used because of the better statistics.
- The widths are driven by lifetime broadening.

Kalkowski, Kaindl, Brewer  
and Krone, PRB 35, 2667 (1987)

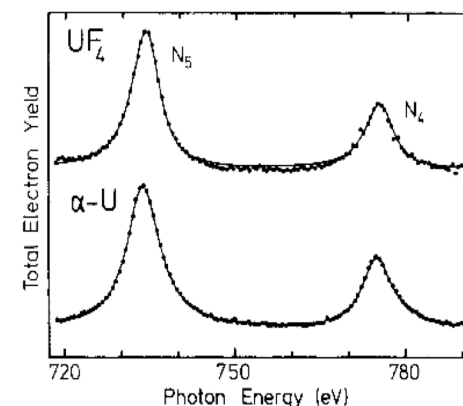
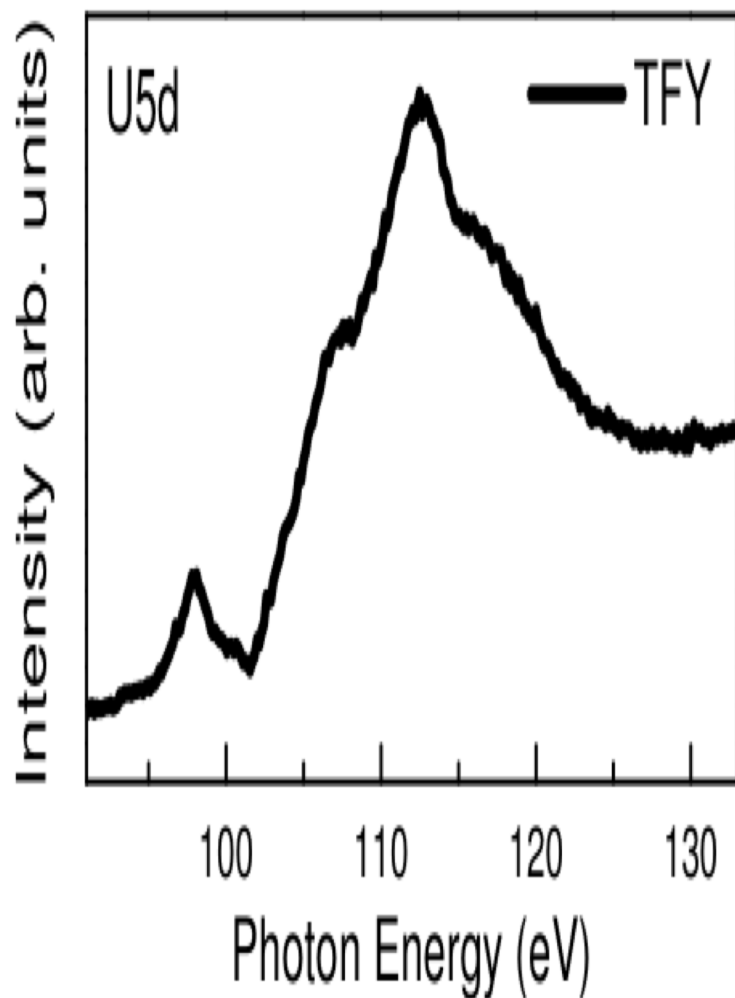


FIG. 7. Total-electron-yield spectra of  $\alpha$ -U metal and  $UF_4$  at the  $N_{4,5}$  thresholds. The solid lines represent fit results.

**Our signal to noise ratio and contamination are worse because of the limitations on sample size at the ALS.**

# U5d XAS: old and new

## Confirmation of Sample Quality



- Our U5d spectrum looks very much like that of KKBK for  $\text{UO}_2$ .
- The photon energy scale of our data was shifted slightly to align with that of KKBK.
- Unlike all of our other U XAS spectra, our U5d was NOT normalized to  $I_0$ .
- TEY: problems again

Kalkowski, Kaindl, Brewer  
and Krone, PRB 35, 2667 (1987)

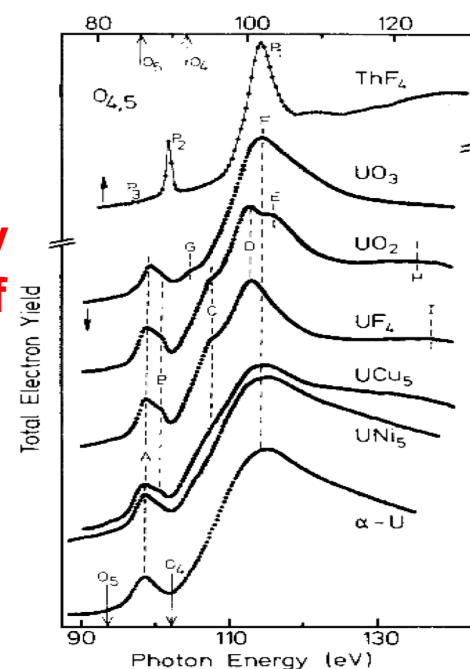
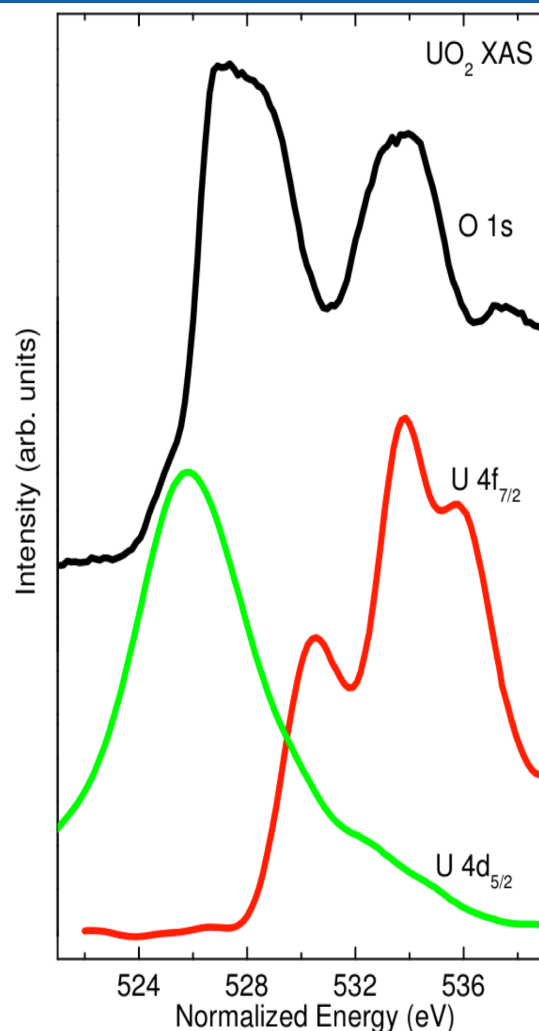


FIG. 8. Total-electron-yield spectra of various U compounds and of  $\text{ThF}_4$  at the  $O_{4,5}$  thresholds. Note the different energy scales for the Th and U spectra; the arrows specify the  $O_4$  and  $O_5$  thresholds from XPS measurements of Th and  $\alpha$ -U metal, respectively (Ref. 46). The various spectral features are explained in the text. The solid lines through the data points serve as guides to the eye.

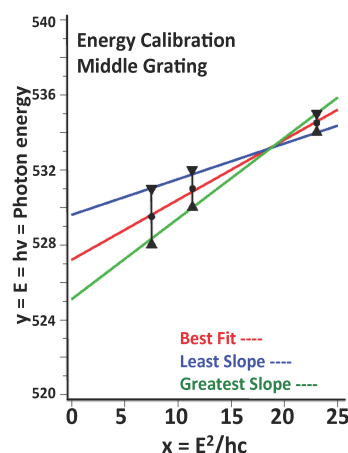


# The XAS spectra can be aligned with the mono calibration and BE correction or by the threshold...



**Colinearity of three points confirms the monochromator calibration.**

**One correction factor:**  
 $\Delta \lambda = 0.3 \text{ \AA}$



## Binding Energy Correction

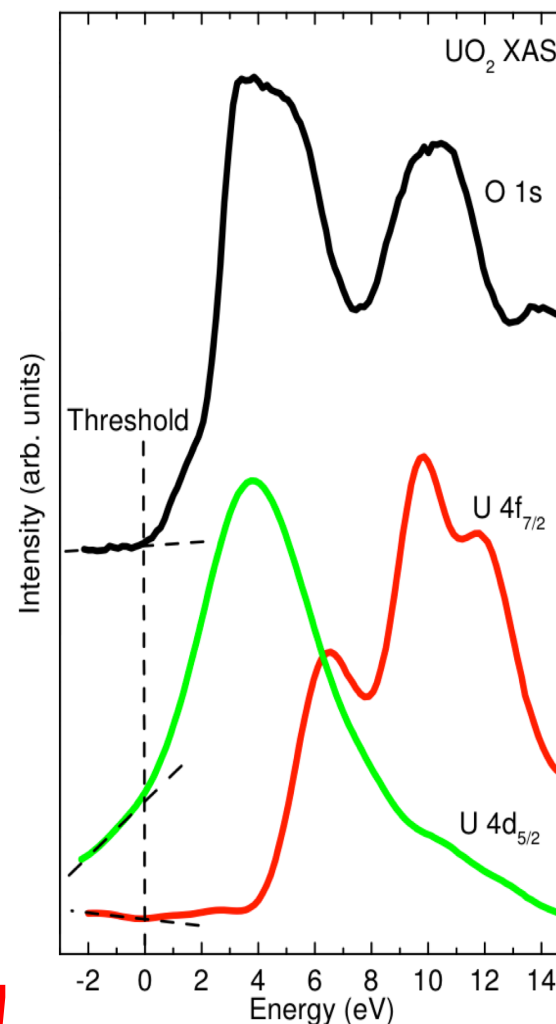
$$NE_{O1s} = h\nu(O1s)$$

$$NE_{U4f} = h\nu(U4f) - [BE(U4f) - BE(O1s)]$$

$$NE_{U4d} = h\nu(U4d) - [BE(U4d) - BE(O1s)]$$

**U-XAS smoothed slightly.**

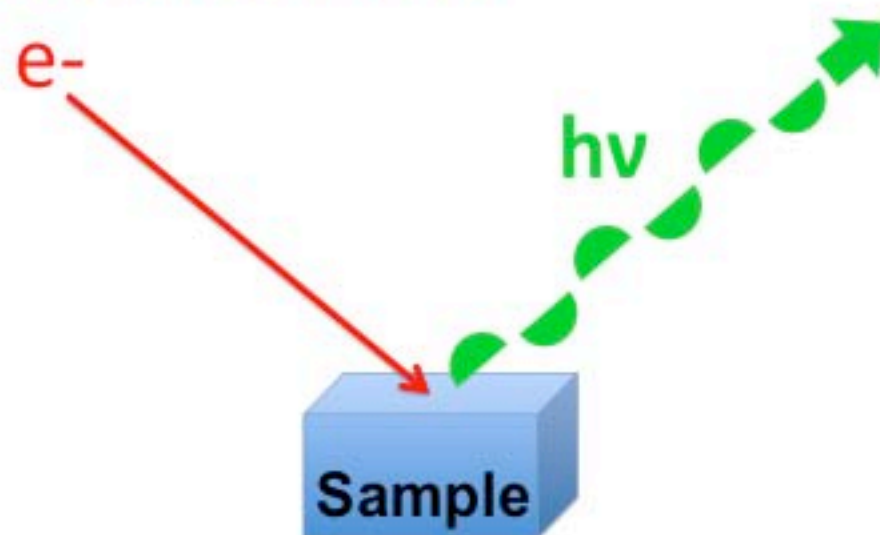
**Either way, the result is the same!**







**Mono-energetic  
beam of electrons**



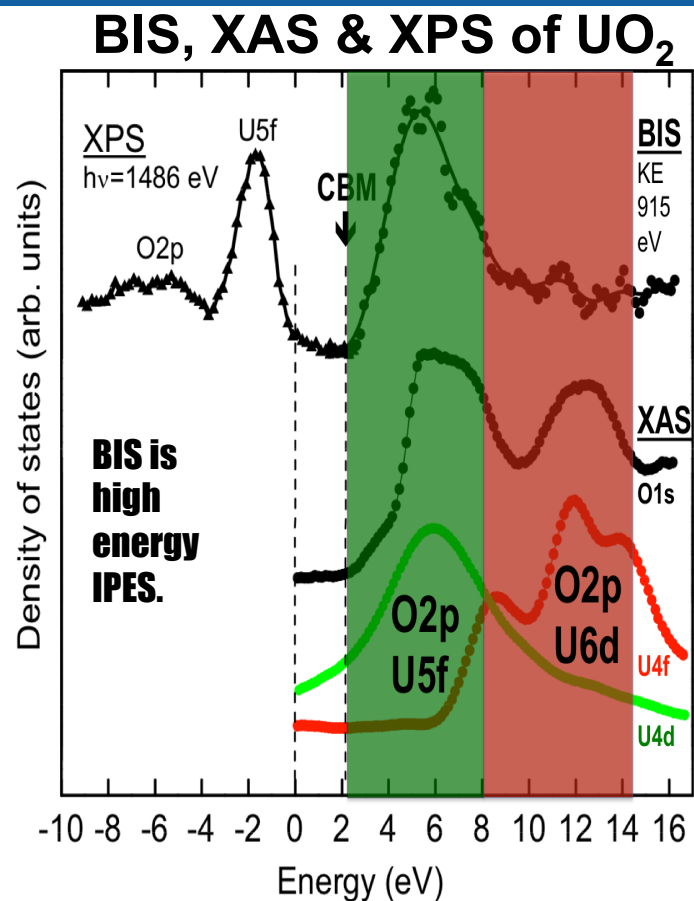
**Wavelength  
selection in  
detection of  $h\nu$**

**Can also do  
XES with  
photon in &  
photon out**

**IPES**       $h\nu = KE_e - H^F + \Phi$

**XES**       $KE_e > BE(\text{core}) \text{ \& } h\nu \approx BE(\text{core})$

# A confirmation can be obtained from BIS and IPES.



- The BIS spectrum will be dominated by the 5f contribution, because the 5f Cross section is about 10x the 6d Cross section. [Yeh and Lindau, At. Data Nucl. Data Tables 32, 99 (1985).]

- At the lowest energies, a weak 6d state can be seen in the IPES of Chauvet and Baptist, Solid State Commun. 43, 793 (1982).

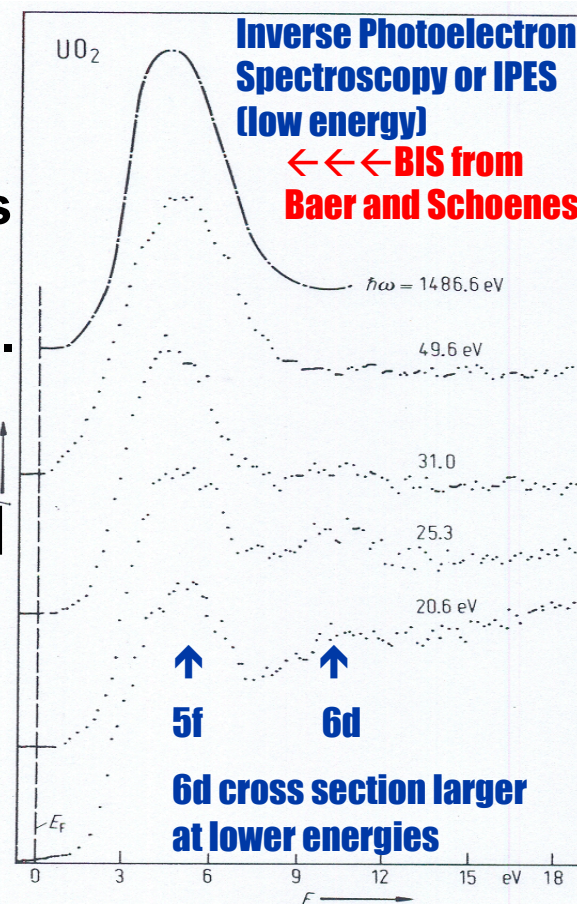


Fig. 117.  $\text{UO}_2$ . Inverse photoemission (BIS) spectra recorded for different photon energies:  $h\omega = 20.6 \dots 49.6$  eV [82C2] and  $h\omega = 1486.6$  eV [80B3].

**The Conduction Bands can be separated experimentally into U5f-O2p and U6d-O2p parts!**

# XAS of Pu

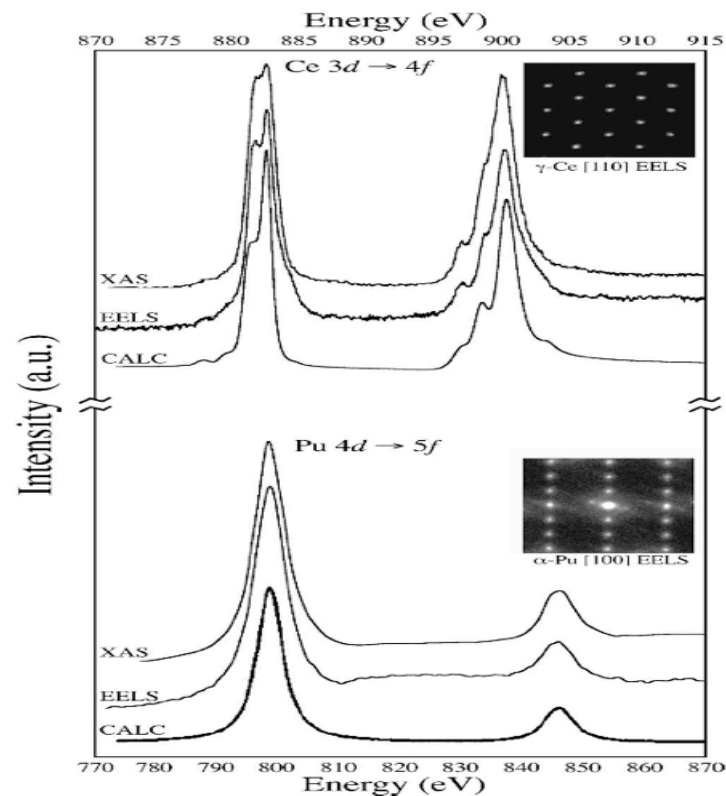
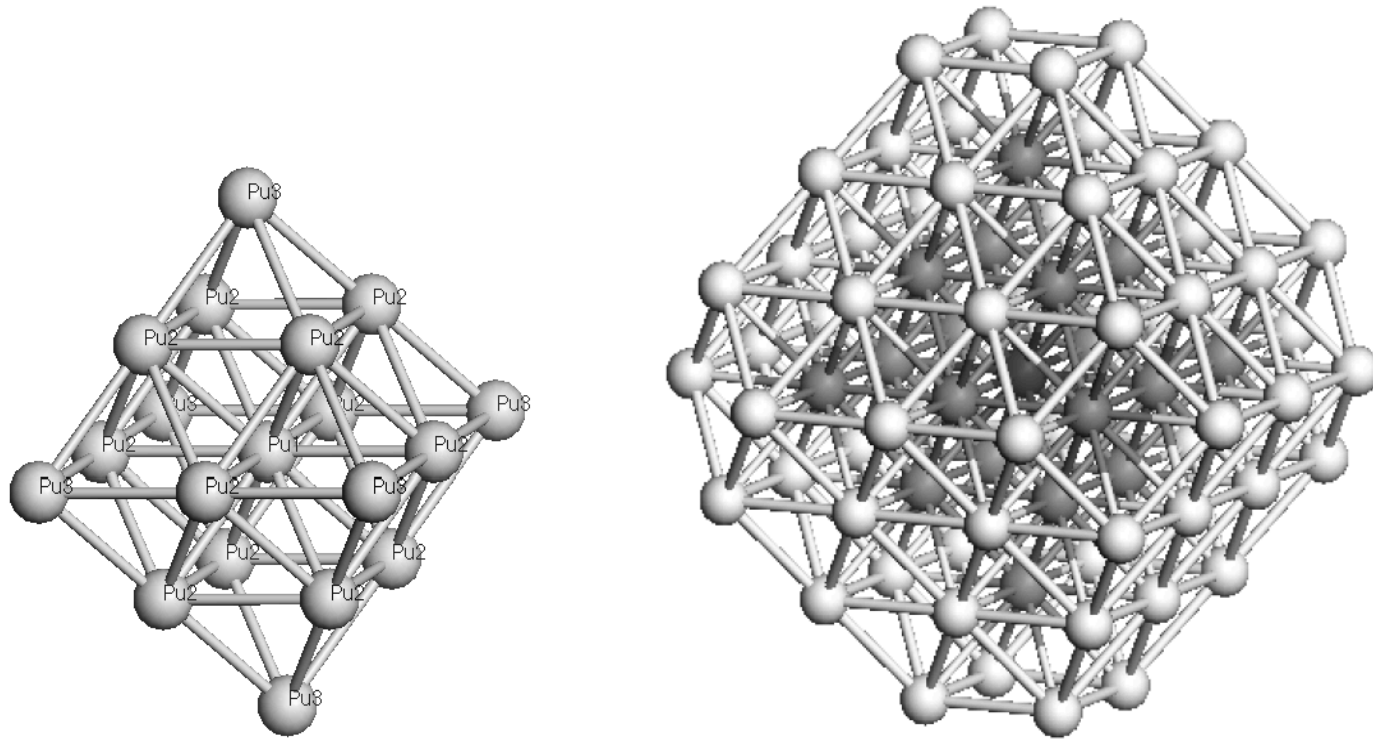


FIG. 2. White line spectra  $\alpha$ -Pu ( $N_{4,5}, 4d \rightarrow 5f$ ) and Ce ( $M_{4,5}, 3d \rightarrow 4f$ ) acquired by EELS in a TEM, XAS, and spectral simulation are shown here. A single-crystal diffraction pattern from each metal is presented, confirming the phase being examined by EELS. For Ce, the  $3d_{5/2}$  peak is near 884 eV and the  $3d_{3/2}$  peak is near 902 eV. For Pu, the  $4d_{5/2}$  peak is near 798 eV and the  $4d_{3/2}$  peak is near 845 eV (Ref. 14). Note the significantly different energy scales for Ce and Pu.

- J. G. Tobin, K. T. Moore, B. W. Chung, M. A. Wall, A. J. Schwartz, G. van der Laan, and A. L. Kutepov, Phys. Rev. B **72**, 085109 (2005).

# Pu Clusters

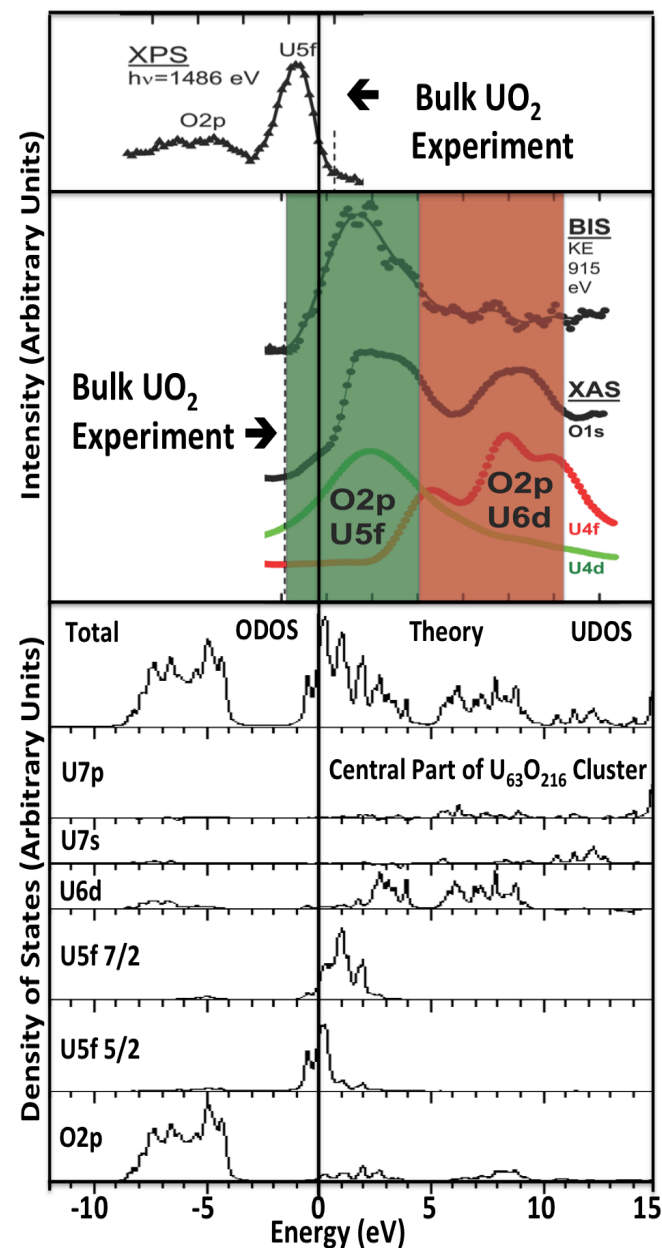


The structures of  $\delta$ -Pu-like  $\text{Pu}_{19}$  and  $\text{Pu}_{79}$  clusters are shown here. The  $\text{Pu}_{79}$  cluster contains a  $\text{Pu}_{19}$  cluster as a “core” (showed as the dark spheres). Pu1 is the central atom of the  $\text{Pu}_{19}$  cluster: twelve Pu2 and six Pu3 atoms form its nearest neighbors and the next nearest neighbors, respectively.



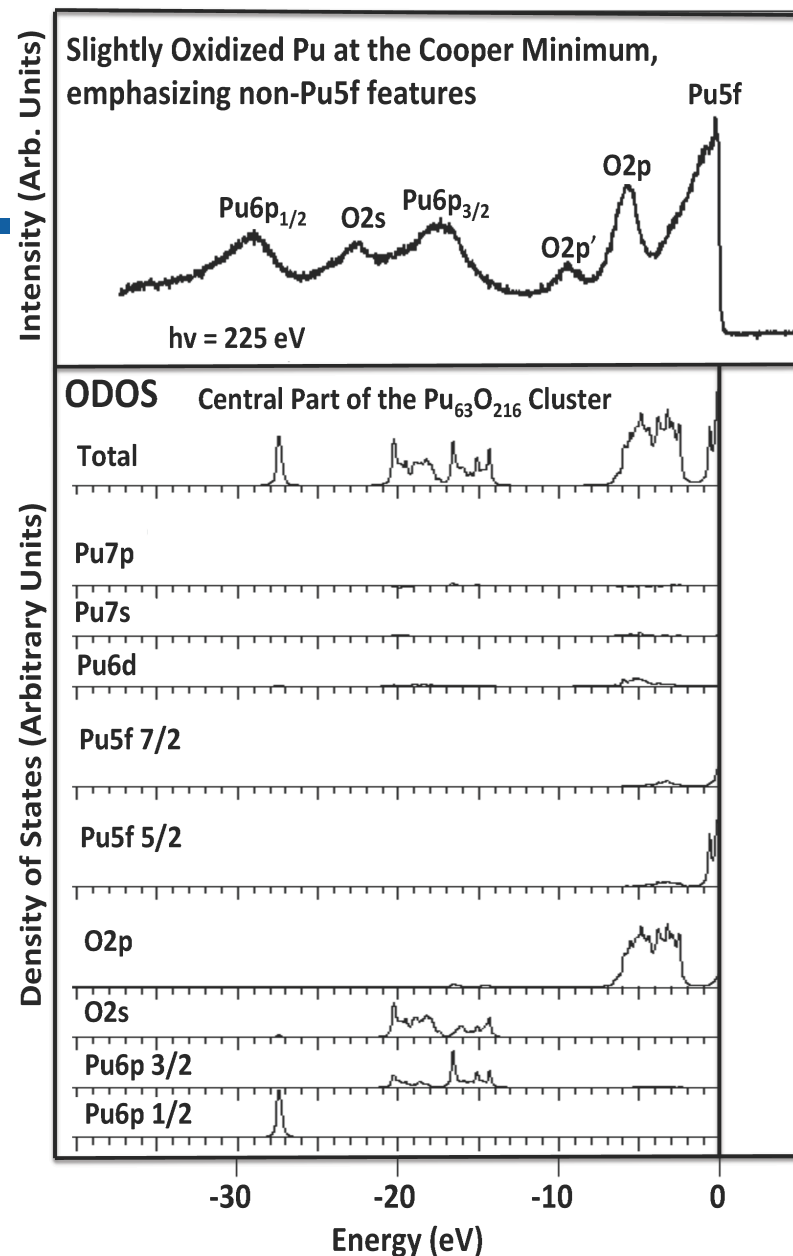
# Comparison to UO<sub>2</sub> Clusters

A comparison of the Density of States (DOS) for the central part of a U<sub>63</sub>O<sub>216</sub> cluster with spectroscopic results from a bulk UO<sub>2</sub> sample. The Occupied Density of States (ODOS) is compared to the data from X-ray Photoelectron Spectroscopy (XPS). The Unoccupied Density of States (UDOS) is compared to the X-ray Absorption Spectroscopy (XAS) and Bremsstrahlung Isochromat Spectroscopy (BIS) data. Partial and total DOS are provided. The spectroscopic data are representative of experimental DOS estimates, although skewed by cross-sectional effects.



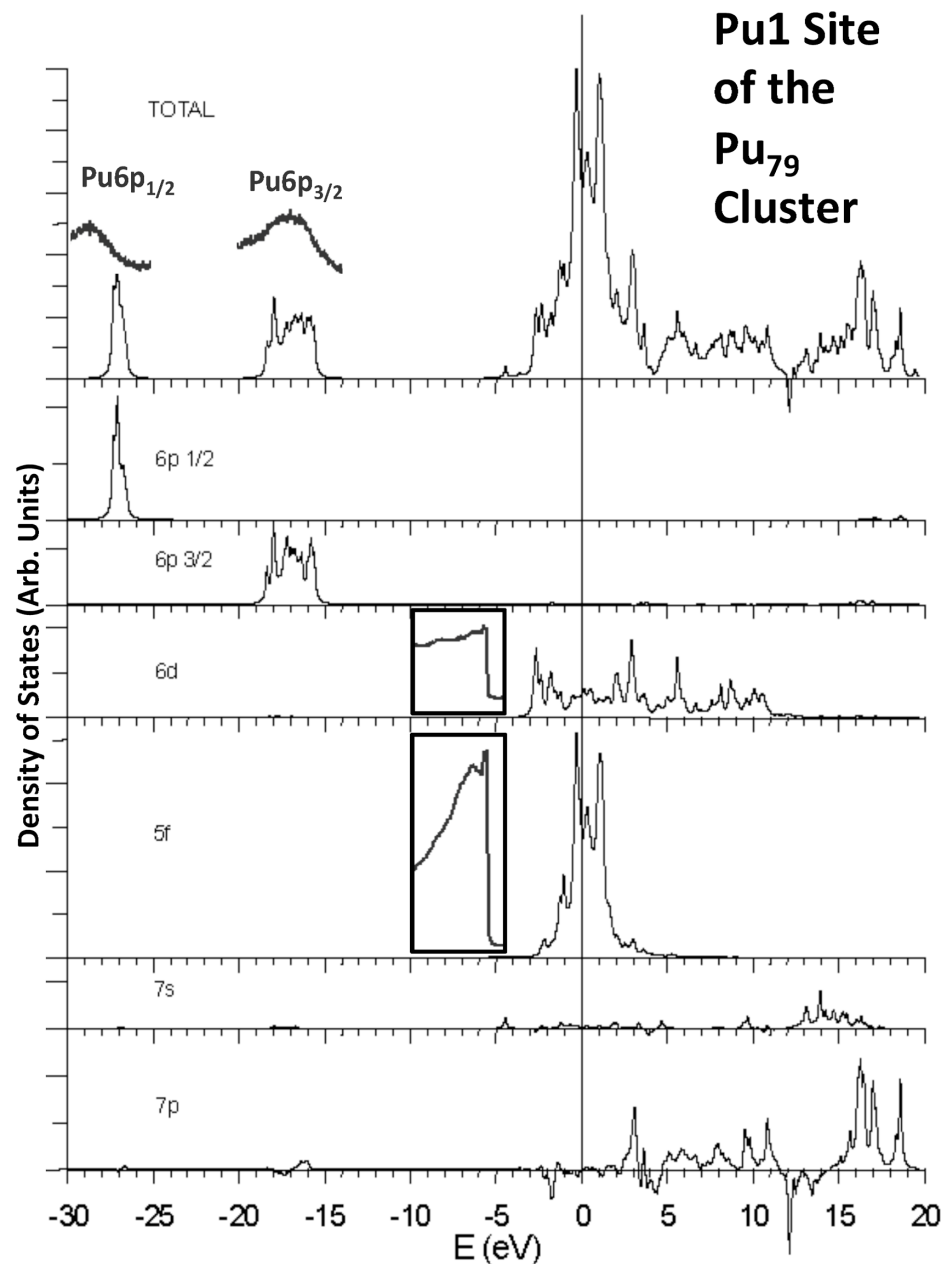
# Comparison to PuO<sub>2</sub> Clusters

A comparison of the Density of States (DOS) for the central part of a Pu<sub>63</sub>O<sub>216</sub> cluster with spectroscopic results from a slightly oxidized bulk Pu sample. The Occupied Density of States (ODOS) is compared to the data from synchrotron-radiation-based Photoelectron Spectroscopy (PES). Partial and total DOS are provided. The spectroscopic data are representative of experimental DOS estimates, although skewed by cross-sectional effects. By working at the Cooper Minimum, the non-5f features are emphasized.



# Comparison to Pu Clusters

Total and partial densities of states for the central atom Pu1 of a  $\text{Pu}_{79}$  cluster. (light lines) Spectroscopic results from a slightly oxidized bulk Pu sample are also shown here. (heavy lines in insets). The spectroscopic data are representative of experimental DOS estimates, although skewed by cross-sectional effects. The two 6p experimental peaks, taken at the Cooper Minimum with  $h\nu = 225$  eV, are shown at their measured binding energies, vertically offset above the total spectrum. The near Fermi edge region, collected on resonance at  $h\nu = 125$  eV to strongly emphasize the 5f character, is shown in the inset, horizontally offset from the calculated 5f peak. Similarly, the near Fermi edge region, collected at anti-resonance at  $h\nu = 100$  eV to strongly emphasize the 6d character, is shown in the inset, horizontally offset from the calculated 6d peak.



# Conclusion



Using spectroscopic data produced in the experimental investigations of bulk systems, including X-Ray Absorption Spectroscopy (XAS), Photoelectron Spectroscopy (PES) and Bremsstrahlung Isochromat Spectroscopy (BIS) <sup>1-5</sup>, the theoretical results within for UO<sub>2</sub><sup>6</sup>, PuO<sub>2</sub><sup>6</sup> and Pu<sup>7</sup> clusters have been evaluated. The calculations of the electronic structure of the clusters have been performed within the framework of the Relativistic Discrete-Variational Method (RDV).<sup>6,7</sup> The comparisons between the LLNL experimental data and the Russian calculations are quite favorable. The cluster calculations may represent a new and useful avenue to address unresolved questions within the field of actinide electron structure, particularly that of Pu. Observation of the changes in the Pu electronic structure as a function of size suggests interesting implications for bulk Pu electronic structure.

1. J.G. Tobin and S.-W. Yu, Phys. Rev. Lett, **107**, 167406 (2011).
2. S.-W. Yu, J. G. Tobin, J. C. Crowhurst, S. Sharma, J. K. Dewhurst, P. Olalde-Velasco, W. L. Yang, and W. J. Siekhaus, Phys. Rev. B **83**, 165102 (2011).
3. J.G. Tobin, B.W. Chung, R. K. Schulze, J. Terry, J. D. Farr, D. K. Shuh, K. Heinzelman, E. Rotenberg, G.D. Waddill, and G. Van der Laan, Phys. Rev. B **68**, 155109 (2003).
4. J.G. Tobin, P. Söderlind, A. Landa, K.T. Moore, A.J. Schwartz, B.W. Chung, M.A. Wall, J.M. Wills, R.G. Haire, and A.L. Kutepov, J. Phys. Cond. Matter **20**, 125204 (2008).
5. S.-W. Yu, J. G. Tobin, P. Olalde-Velasco, W. L. Yang, and W. J. Siekhaus, J. Vac. Sci. Tech. A. **30**, 011402 (2012).
6. M.V. Ryzhkov and A.Ya. Kupryazhkin, J. Nucl. Materials **384**, 226 (2009).
7. M.V. Ryzhkov, A. Mirmelstein, S.-W. Yu and J.G. Tobin, "Probing Actinide Electronic Structure through Pu Cluster Calculations," submitted to Phys. Rev. B, Feb 2012.